Measurement of Mass Diffusivity Using Interferometry through Sensitivity Analysis

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ABSTRACT: Mass diffusion of a solute in a solvent is realized in many applications. The extraction of transport properties from optical images has not received sufficient attention, though refractive index techniques for determination of the mass diffusion coefficient of a solute in a binary system have been discussed in the literature. The issue becomes important in experiments involving slow diffusion during which concentration gradients in parts of the domain are large. Accordingly, refractive index gradients are also large and higher order effects influence image formation. This weakness can be addressed by carrying out sensitivity analysis, wherein only that part of the data is analyzed which is highly sensitive to the experimental determination of diffusivity. In the context of interferometry, the present study reports fringe patterns obtained for the diffusion of NaCl and sucrose in deionized water at 25 °C. A Mach–Zehnder configuration of the interferometer has been employed. In an experiment, a layer of solution is placed in a temperature-controlled cavity with fresh water above. The diffusion of the solute into water leads to the formation of time-dependent fringe patterns. The images obtained are analyzed using two different techniques that work with the right combination of fringes. Data analysis is carried out in that region of space and time which is most sensitive to mass diffusivity. The two approaches rely on working with distinguishable fringes in the field of view and their displacement in time. Both of these methods are found to be effective in predicting the mass diffusion coefficient, in fair agreement with the literature. The present work signifies the importance of sensitivity analysis while obtaining reliable values of mass diffusivity using interferometry.

1. INTRODUCTION

The diffusion of species in a mixture is a stochastic process and is known to redistribute matter at a microscopic level. On a macroscopic scale, it follows the gradient diffusion model and is, in principle, completely characterized by Fick’s law leading to a diffusion coefficient, namely, mass diffusivity. The knowledge of mass diffusivity is essential for material characterization, optimal design of unit operations,1,2 and mathematical modeling of various chemical and other engineering processes.3,4 Although an order-of-magnitude determination of a mass diffusivity can be readily obtained using various techniques, improved values of the property, specifically as a function of solute concentration and temperature, require specialized tools. The mass diffusivity of a solute in a solvent, namely a binary system, can be predicted theoretically or determined from empirical correlations.5,6 On the other hand, experimental methods such as quasi-steady-state diffusion through a porous diaphragm,7 Wiener’s method,8 light beam deflection techniques,9,10 decaying pulse technique,11 and interferometry12–16 have also been used to experimentally determine the mass diffusivity. Out of these, optical techniques are of special importance owing to their inertia-free and nonintrusive nature. In this work we present the measurement of mass diffusivity using a Mach–Zehnder interferometer. In particular, we examine two data analysis techniques in the context of interferograms formed in a mass transfer process. We analyze their advantages and disadvantages from a point of view of rigor and possible errors in experimental determination of mass diffusivity. We aid the interferometric determination of mass diffusivity by locating the most sensitive region of space and time, which leads to greater confidence in the parameter measurement procedure.

In an interferometric experiment, diffusion is allowed to progress in time in a reference configuration, such as a rectangular cavity. The binary system is required to be transparent and nonabsorbing. Owing to a gradient in density, properties such as phase and path length of the light beam get altered, which leads to the formation of fringes. The data thus recorded is highly resolved in space and time. Fringes represent the concentration field in the spatiotemporal domain from which diffusivity can be obtained experimentally. In the literature, various interferometric techniques have been employed to measure mass diffusivity. Guo et al.17 used phase shifting interferometry to determine the diffusion coefficient of NaCl solution in water as a function of salt concentration. The concentration field was obtained by counting the number of fringes. Torres et al.18 employed a phase shifting technique to determine the mass diffusivity of 10 mg/mL solution of NaCl and 400 mg/mL solution of sucrose in water using a small (3 mm × 20 mm × 45 mm) diffusion cell. Interestingly, usage of a small cavity facilitated the formation of fewer fringes and the experimental determination of mass diffusivity within a short period of 10–13 min with an uncertainty of 5%. Riquelme et al.19 carried out interferometric measurement of the diffusion coefficient by using electronic...
obtained a maximum uncertainty of 0.4 ± 0.001 m²/s at 25 °C. The methods were based on analyzing horizontal fringes obtained by subtracting digitized speckled images of the test cell corresponding to a pair of time instants and curved fringes for which one arm of the interferometer was tilted slightly between the two exposures. Riquelme et al.14 reported a maximum uncertainty of 5−6% in diffusivity. Rard et al.19 calculated the fixed volume diffusion coefficient of NaCl solution from dilute to high concentrations (0.5−23 wt %) by Rayleigh interferometry and obtained a maximum uncertainty of 0.4−0.7% in the diffusion coefficient. Chang et al.20 used Gouy interferometry to obtain the diffusion coefficient of supersaturated solution of NaCl (4−24.2 wt %). Their diffusivity values agree within ±3% with the data reported by Rard et al.19. The authors emphasized the importance of optical techniques for overcoming errors when diffusivity data of unsaturated solutions is extrapolated to the supersaturated regime. The studies of Rard19 and Chang20 are aimed at determining diffusivity in concentrated solutions. A comparison of interferometric techniques to measure the mass diffusivities of NaCl and sucrose over a broad range of concentrations and temperatures is given in Table 1.

Apart from optical techniques, three other techniques, namely, the diaphragm cell technique, conductometric method, and Taylor dispersion method, have frequently been used to measure the binary diffusion coefficient. In a diaphragm cell, the integral diffusion coefficient is obtained for a short duration experiment with concentration c on the solution side and pure water on the other. The integral diffusion coefficient is interpreted as $D_i = (1/c) \int_c^1 D \, dc$, where $D$ is the true differential diffusion coefficient that would be measured by optical or conductometric methods with small concentration differences.21 Rard and Miller21 reported that the conversion of an integral diffusion coefficient into the desired differential diffusion coefficient leads to a large uncertainty. Breer et al.7 examined the diaphragm cell technique using lower concentrations of NaCl and KCl in order to reduce the errors associated with the analysis of initial and final concentration differences and their influence on the diffusivity evaluation. With a conductometric method, Lobo et al.22 obtained the diffusion coefficients of 0.001−1 M KCl solutions with standard deviations of 0.01−0.05%. Here, the ratio of electrical resistances of the electrolyte solution was measured with time using an ac transformer bridge. The ratio was measured from two vertically opposed capillaries closed at one end by a platinum electrode and positioned above the other, with the open ends separated by a small distance. The open ends were suspended throughout the experiment in a solution with concentration equal to the average of the initial solute concentrations. However, density distribution during experiments that can increase error.

An overview of the literature, where interferometric techniques are used to determine the mass diffusion coefficient, suggests that mostly short duration experiments were conducted on small volume samples and over a limited range of solute concentrations. However, density distribution measured to determine diffusivity may not be sufficiently sensitive to the values of diffusivity. Consequently, the measured values of diffusivity are prone to errors. In the present study, we carry out measurements in the bulk of the solution with a large sample volume (0.6 L) and broad initial

### Table 1. Mass Diffusion Coefficients of Various Solute–Solvent Systems from the Literature

<table>
<thead>
<tr>
<th>binary system</th>
<th>wt %</th>
<th>temp (°C)</th>
<th>$D$ (×10^{-9} m²/s)</th>
<th>name of technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>sucrose + H₂O</td>
<td>3</td>
<td>22</td>
<td>0.412</td>
<td>Wiener’s method⁹</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td></td>
<td>0.522</td>
<td>Stokes–Einstein equation⁶</td>
</tr>
<tr>
<td>glucose + H₂O</td>
<td>1.77</td>
<td>25−39</td>
<td>0.651−0.924</td>
<td>Taylor dispersion method²³</td>
</tr>
<tr>
<td>lactose + H₂O</td>
<td>3.3</td>
<td>25−55</td>
<td>0.541−1.018</td>
<td>Taylor dispersion method²³</td>
</tr>
<tr>
<td>fructose + H₂O</td>
<td>1.77</td>
<td>25−39</td>
<td>0.661−0.915</td>
<td>Taylor dispersion method²³</td>
</tr>
<tr>
<td>NaCl + H₂O</td>
<td>3−5</td>
<td>18−30</td>
<td>1.2−1.8</td>
<td>decaying pulse technique¹¹</td>
</tr>
<tr>
<td></td>
<td>9.27</td>
<td>26</td>
<td>1.58−1.602</td>
<td>ESPI¹⁴</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>25</td>
<td>1.507</td>
<td>phase shift interferometry¹⁷</td>
</tr>
<tr>
<td></td>
<td>0.5−23</td>
<td>25</td>
<td>1.48−1.57</td>
<td>Rayleigh interferometry¹⁹</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>25</td>
<td>1.49</td>
<td>ref 28</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>25</td>
<td>1.474</td>
<td>diaphragm cell⁷</td>
</tr>
<tr>
<td></td>
<td>0.001</td>
<td>25</td>
<td>1.42−1.59</td>
<td>phase shift interferometry¹⁸</td>
</tr>
<tr>
<td></td>
<td>0.5−24.2</td>
<td>25</td>
<td>1.47−1.58</td>
<td>Gouy interferometry²⁰</td>
</tr>
<tr>
<td></td>
<td>5−26</td>
<td>25</td>
<td>1.325−1.5</td>
<td>present work</td>
</tr>
<tr>
<td>KCl + H₂O</td>
<td>5.1</td>
<td>18.6−30.2</td>
<td>1.72−2.14</td>
<td>decaying pulse technique¹¹</td>
</tr>
<tr>
<td></td>
<td>7−24.9</td>
<td>25</td>
<td>1.89−2.197</td>
<td>Rayleigh interferometry¹⁹</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Gouy interferometry²⁰</td>
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<td></td>
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<td></td>
<td>conductometric method²²</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>diaphragm cell⁷</td>
</tr>
</tbody>
</table>
The test cell has a nominal diameter (distance between two opposite faces of the octagon) of 130.6 mm and a height of 50 mm.

The cavity volume thus created is around 0.6 L. The cavity aspect ratio, defined as the diameter to height ratio, is 2.61. The size of the cavity in the direction of passage of the light beam, namely its diameter, plays an important role in fixing the resolution of the concentration measurement. The larger the diameter of the test cell, the greater is the resolution and the number of fringes in an experiment. It minimizes errors arising from end effects generated by a temperature difference across the optical window. The cavity diameter is also the imaging dimension in the viewing direction. If it is excessively large, refraction errors can be substantial, calling for higher order corrections in the interferogram analysis. The expression for density change per fringe shift including refraction effects has been shown to be \(^{26}\)

\[
\lambda = \Delta \rho \sigma L \frac{dn}{d\rho} + \frac{1}{6n} \left( \frac{dn}{dy} \right)^2 \left[ \left( \frac{dp}{dy} \right)_u - \left( \frac{dp}{dy} \right)_b \right]^2 L^3
\]  

The first term in eq 1 is related to the optical path difference, and the second term is due to refraction. For the data within the sensitivity window, the second term was estimated to be less than 1% of the wavelength. Hence, it has been neglected. The above discussion therefore clearly suggests that the size of the apparatus is large enough to enhance the resolution, but small enough to neglect the refraction errors. The solution in the test and the reference cells is confined by two copper plates, 2 mm thick, above and below. The cavity through which the laser beam passes is made of 50 × 50 mm\(^2\) optical windows made of BK-7 material with \(\lambda/4\) surface flatness and 30–40 scratch–dig surface quality. Parallelism of the optical windows is established by requiring the test and reference beams to interfere constructively with a clear bright patch formed at the center of the screen. The top and bottom surfaces of the cavity are maintained at uniform temperatures by circulating water from a constant temperature bath. The wall temperatures are monitored by surface mounted thermocouples connected to a multichannel temperature recorder (DBK scanner). The room temperature is maintained constant within ±0.2 °C. The cavities are covered by a 4 mm thick Bakelite sheet in order to insulate the test section from the atmosphere.
ment is particularly relevant when the diffusion coefficient is to be determined at elevated temperatures.

At the start of the experiment, the test and the compensation chambers are filled with ultrapure Millipore water. The temperature of water in the two sections is maintained at 25 ± 0.1 °C over the duration of the experiment by running the constant temperature bath. Subsequently, the path lengths of the test and reference beams are balanced by examining the infinite fringe setting formed on the screen. The image is a bright patch with the number of fringes being zero. For temporal stability the interferometer was mounted on pneumatic legs to avoid possible building vibrations during experiments. The interferometer alignment was checked before and after the experiment by its ability to reproduce the initial undisturbed “infinite fringe setting”. A known quantity of concentrated solution is added at the base of the cavity by a syringe until air gaps are eliminated and the test cell is full. The time elapsed for starting the experiment is 2–4 min, which is small compared to 40–50 h required for the diffusion process to fully evolve in the fluid medium. Once the solute is introduced, mass diffusion commences immediately and fringes start appearing in the field of view. Instantaneous snapshots of interferograms are recorded at 30 min intervals using the CCD camera connected to the computer. The duration of the experiment is ascertained from sensitivity considerations and is discussed in section 4. The two solutes, namely NaCl and sucrose, were procured from Thermo Fisher Scientific India Pvt. Ltd. (each of impurity 0.005% or less). We also measure the refractive index as a function of the concentrations of sucrose and salt in water using a refractometer (Anton Paar-Abbeomat S00).

3. Theory and Data Analysis

The principle on which a Mach–Zehnder interferometer works is based on the dependence of the refractive index on the density of a transparent medium, namely, the Lorenz–Lorentz relationship[4,27] given by

$$\frac{1}{\rho} \frac{d n}{d \rho} = \varepsilon_M$$

(2)

where \( n \) is the refractive index, \( \rho \) is the density, and \( \varepsilon_M \) is a material property that can be a function of the wavelength of light. Fringes are formed by the superposition of the wave fronts passing through the test and reference sections. Since both sections are held under isothermal conditions, mass diffusion in the test cell creates a refractive index gradient perpendicular to the path of the test beam, giving rise to a fringe pattern. Since a minimum in the intensity of light in a fringe is a curve of constant refractive index, it is also a locus of constant phase, density, and species concentration. Therefore, the fringe distribution can be analyzed to obtain a concentration distribution in the test cell. The change in the density between the two consecutive fringes, \( \Delta \rho \), is obtained using the principle of wave optics given by[4,27]

$$\Delta \rho = \frac{\lambda L}{\partial n/\partial \rho}$$

(3)

Here \( dn/\partial \rho \) is the gradient of the refractive index with respect to density and is a property specific to the choice of the solute and the solvent, \( L \) is the length of the apparatus in the viewing direction, and \( \lambda \) is the wavelength of light.

In eq 3, \( L \) is apparatus specific while \( \lambda \) depends on the laser source. The gradient of the refractive index, \( dn/\partial \rho \), on the other hand, is a material property, which we measure using a refractometer. In Figure 2 we plot the refractive index as a function of concentration (density) for both sucrose and salt, from which \( dn/\partial \rho \) can be easily obtained. It should be noted that eq 3 assumes the passage of the light beam to be straight. However, errors may be induced due to bending of the beam because of a variable refractive index field. The errors originating from this effect are estimated to be less than 1% with reference to eq 1, for the experimental data considered in the present analysis. The details of this effect have been discussed elsewhere.[24,25]

A schematic of the diffusion cell employed in the present work is shown in Figure 3a, where the total cell height is \( H \), while the solute height at the beginning of the experiment \((t = 0)\) is \( h_1 \). The concentration profile along the vertical coordinate \((y\text{-axis})\) of the test cell is obtained as a function of time by applying the species mass balance equation jointly with Fick’s law of diffusion in the homogeneous media. Considering the mass diffusion coefficient \( D \) to be a constant, the governing equation for the density distribution \( \rho(y,t) \) in the test cell can be written as

$$\frac{\partial^2 \rho}{\partial y^2} = \frac{1}{D} \frac{\partial \rho}{\partial t} \quad 0 < y < H, \quad t > 0$$

(4)

Since the boundaries of the cavity are impermeable to mass transfer, we have

$$\frac{\partial \rho}{\partial y} = 0 \quad \text{at } y = 0 \text{ and } y = H \text{ for } t \geq 0$$

(5)

Let \( \rho_1 \) be the highest density of the concentrated solution and \( \rho_0 \) be the density of the solvent. Consequently, the initial condition corresponds to

$$\rho = \rho_1 \quad \text{for } 0 < y < h_1$$

$$\rho = \rho_0 \quad \text{for } h_1 < y < H \text{ at } t = 0$$

(6)

Nondimensionalizing eq 4 by substituting \( \tau = Dt/H^2 \), \( \eta = y/H \), \( \kappa = h_1/H \), and \( \theta = (\rho - \rho_0)/(\rho_1 - \rho_0) \), we get

$$\frac{\partial^2 \theta}{\partial \eta^2} = \frac{\partial \theta}{\partial \tau} \quad \text{for } 0 < \eta < 1$$

(7)
where the dimensionless initial and boundary conditions become

\[ \theta = 1 \quad \text{for} \ 0 < \eta < \kappa \]
\[ \theta = 0 \quad \text{for} \ \kappa < \eta < 1 \quad \text{at} \ \tau = 0 \]  
\[ \frac{\partial \theta}{\partial \eta} = 0 \quad \text{at} \ \eta = 0 \quad \text{and} \ \eta = 1 \quad \text{for} \ \tau \geq 0 \]  

Equation 7 can be solved analytically for the mentioned boundary and initial conditions by a method of separation of variables as leading to an analytical solution given by

\[ \theta = \kappa + \frac{2}{\pi} \sum_{m=1}^{\infty} \left\{ \frac{1}{m} \exp\left(-m^{2} \pi^{2} \tau\right) \cos(m \eta) \sin(m \kappa) \right\} \]  

Equation 10 gives the variation of concentration as a function of time and space.

In Figure 4 we plot the dimensionless concentration (density) \( \theta \) as a function of the dimensionless length scale \( \eta \) at various time intervals. It can be seen that, at very small times, there is a sharp gradient at the interface location \( y = h_{1} \). However, with the increase in time, diffusion of both species away from the interface diminishes the gradient gradually while keeping the concentration at \( y = h_{1} \) constant at the average value for a prolonged period of time. In the inset of Figure 4 we plot concentration at \( y = h_{1} \) as a function of time. The inset indeed shows that the concentration at the initial interface remains at \( \theta = 0.5 \) for a considerable length of time. Furthermore, the time over which \( \theta \) remains constant at 0.5 can be seen to be increase with \( h_{1} \).

Since the concentration of solute at \( y = h_{1} \) remains constant for a long period, eq 10 can be solved only in the region \( h_{1} < y < H \) by considering a constant concentration boundary condition at \( y = h_{1} \) and no flux boundary condition at \( y = H \).

We describe this diffusion field in Figure 3b along with the boundary conditions given by

\[ \rho_{\eta} = 0, \ \tau \geq 0 \]  
\[ \rho = \rho_{c}, \ 0 < t < t_{1} \]  

\[ \rho = \rho_{0}, \ 0 < t < t_{1} \]  

Equation 11 gives the variation of concentration as a function of position along the vertical coordinate of the test cell. \( I \) is the point of intersection of the curves where the solute concentration is practically equal to 0.5. The inset shows the plot of concentration (\( \theta \)) with time (\( \tau \)) for various interface thicknesses. As the thickness increases, the dimensionless concentration remains constant at 0.5 for a longer time period.

\[ \rho = \rho_{1} \quad \text{at} \ y = h_{1} \quad \text{for} \ 0 < t < \bar{t} \]  
\[ \frac{\partial \rho}{\partial y} = 0 \quad \text{at} \ y = H \quad \text{for} \ \tau \geq 0 \]  

Here \( \bar{t} \) is the time interval over which the concentration at \( y = h_{1} \) remains constant as shown in the inset of Figure 4. The initial condition is prescribed as

\[ \rho = \rho_{0} \quad \text{for} \ h_{1} < y < H \quad \text{at} \ t = 0 \]  

If we define nondimensional parameters as \( \tau_{1} = D t / (H - h_{1})^{2} \), \( \eta_{1} = (y - h_{1}) / (H - h_{1}) \), and \( \theta_{1} = (\rho - \rho_{1}) / (\rho_{0} - \rho_{1}) \), the analytical solution of eq 10 for the mentioned initial conditions

\[ \theta_{1} = 1 \quad \text{for} \ 0 < \eta_{1} < 1 \quad \text{at} \ \tau_{1} = 0 \]  

and boundary conditions

\[ \rho_{\eta} = 0, \ \tau_{1} \geq 0 \]  
\[ \rho = \rho_{c}, \ 0 < t_{1} < \tau_{1} \]  
\[ \rho = \rho_{0}, \ 0 < t_{1} < \tau_{1} \]  

Figure 3. Initial configuration of a binary mass diffusion process in a cavity with concentration boundary conditions. (a) Boundary conditions specified at top and bottom of the cavity (\( y = 0 \) to \( H \)) lead to eq 10, while (b) boundary conditions specified at the top of the cavity and the interface between solute and solvent (shaded area from \( y = h_{1} \) to \( H \)) lead to eq 15. (c) Schematics of assumption made for displacement of fringe (\( \delta \)) from constant position to obtain eq 19.
In this work, we determine mass diffusion. In order to overcome this shortcoming, a part of the unsteady data set that shows the density distribution is obtained. We have carried out this process of sensitivity analysis by fitting the analytical solution given by eq 15 with the measured concentration of species from the interferometry experiments. In order to carry out regression, the error functional \( \epsilon \) is defined as

\[
\epsilon = \sum_{i=1}^{N} (\rho_{a,i}(y) - \rho_{a,i}(y_i; D))^2
\]

where subscripts "a" and "m" indicate experimentally and analytically obtained values. The error thus determined depends on the diffusion coefficient \( D_0 \); the best value of \( D_0 \) is the one that minimizes error in eq 16. As the mass transfer process approaches steady state, eq 15 becomes less sensitive to the variation of \( D_0 \), and therefore the error minimization process does not yield the best value of \( D_0 \). In order to overcome this shortcoming, a part of the unsteady data set that shows the greatest dependence on the diffusion coefficient needs to be obtained. We have carried out this process of sensitivity analysis in section 4.

We have employed two approaches to determine mass diffusivity, based on how the fringe patterns are analyzed. In the first approach, the fringe patterns are used to obtain a frame-wise density distribution \( \rho(y,t) \) at various time instants. The positions of the fringes are extracted from interferograms with the help of peaks and valleys in the position-intensity plot. A MATLAB program was written for this purpose. Density distribution is obtained by sequentially adding \( \Delta \rho_s := \sum_{i=1}^{m} (\rho_{a,i}(y) - \rho_{a,i}(y_i; D)) \) to that of water. Fringes close to the interface cannot be analyzed owing to lack of resolution and large refraction errors. These are excluded by considering only those fringes in the space and time domain for which the sensitivity coefficient is large (section 4). The density data thus obtained leads to \( \rho_{s,e} \), while that from eq 15 yields \( \rho_{s,m} \). Substitution in eq 16 finally leads to the diffusion coefficient for which \( \epsilon \) is a minimum. This approach is referred to in the following discussion as full fringe analysis.

The second approach studied in the present work is an approximate method to determine mass diffusivity aimed toward computational simplicity and speed of analysis. It should be noted that, in the analytical solution given by eq 15, the coefficient of each term in the sum is weighed by \( 1/(2m + 1) \), while the exponential term in the sum has a coefficient \( -(2m + 1)^2/4 \). Consequently, for a given \( r_u \), the value of the second term \( (m = 1) \) is expected to be significantly smaller than the first term \( (m = 0) \). In order to simplify the analysis, we consider only the first term of eq 15 associated with \( m = 0 \) and \( \theta_i \) as a constant associated with a fringe of interest. The corresponding approximate solution can then be written as

\[
\theta_i \approx \frac{4}{\pi} \exp \left\{ -\frac{\pi^2}{4} \frac{D_t}{(H - h_i)^2} \right\} \sin \left\{ \frac{\pi}{2} \frac{1}{H - h_i} \right\}
\]

(17)

Here, \( \delta(t) \) is the movement of the fringe from its initial position \( y_i \) over a small time interval for which \( \delta(t)/y_i \ll 1 \) as shown in Figure 3c. In such a limit, eq 17 can be further simplified as

\[
\theta_i \approx \frac{4}{\pi} \exp \left\{ -\frac{\pi^2}{4} \frac{D_t}{(H - h_i)^2} \right\} \sin \left( \frac{\pi}{2} \frac{1}{H - h_i} \right)
\]

(18)

where

\[
X_m = \sin \left( \frac{\pi}{2} \frac{y_i}{H} \right) \cos \left( \frac{\pi}{2} \frac{\delta(t)}{H} \right) + \cos \left( \frac{\pi}{2} \frac{y_i}{H} \right) \sin \left( \frac{\pi}{2} \frac{\delta(t)}{H} \right)
\]

If \( a = \pi \theta_i/4 \), \( b = -\pi^2/4(H - h_i)^2 \), and \( \cos[(\pi/2)(\delta(t)/H)] \cong 1 \), since \( \delta(t) \ll 1 \), eq 18 can be written as

\[
y(t) = y_0 + a \exp(-bDt)
\]

(19)

Here, \( y(t) \) is the position of a particular fringe, while \( y_0, a, \) and \( b \) are model parameters. The mass diffusivity coefficient is a quantity of interest in the measurement. Other parameters depend on the size of the apparatus within which the binary diffusion system is being studied. Parameters \( y_0, a, \) and \( b \) therefore can be determined from a calibration experiment with known species for which the mass diffusivity coefficient \( D_0 \) is known from the literature. A nonlinear regression procedure is required to process the image data \( (\theta_i, y_i, D) \) for the unknown parameters. Once the calibration experiment and parameter estimation are complete, experiments with different samples of solute and solvent can be carried out. The data set \( (\theta_i, y_i, a, b, y_0) \) can now be analyzed for the diffusion coefficient. Interestingly, the number of parameters can be reduced by one if eq 19 is written in terms of a fringe speed \( (dy/dt) \) rather than the location of a fringe.

4. SENSITIVITY ANALYSIS

The sensitivity coefficient arises naturally during the parameter estimation and inverse techniques. It associates the relevance of a measurement with the quantity to be determined. In the present study, measurement of density leads to experimental determination of the binary diffusion coefficient. Consideration of the variation of density over space leads to the sensitivity coefficient associated with the space variable for a consideration of the data over the duration between times \( t_i \) and \( t_2 \), and can be defined as

\[
S_i(\eta_i; D) = \int_{t_1}^{t_2} \frac{d\rho}{dD} \, dt
\]

(20)

In order to nondimensionalize eq 20, we consider \( H - h_i \) to be a characteristic length scale and \( \rho_{s,a} - \rho_{s,b} \) as a characteristic density scale. Dimensionless parameters for the sensitivity function can be defined as

\[
\frac{\sum_{\eta_i} S_i(\eta_i; D)}{D S_i(\eta_i; D)} = \frac{t_i D_1}{(H - h_i)(\rho_{s,a} - \rho_{s,b})}, \quad t_i' = \frac{t_i D_1}{(H - h_i)},
\]

(21)

\[
t_i' = \frac{t_2 D_1}{(H - h_i)^2}, \quad t_{i2} = \frac{(t_2 - t_1) D_1}{(H - h_i)^2}, \quad \xi = \frac{D}{D_i},
\]

and

\[
\eta_i = \frac{y - h_i}{H - h_i}
\]
Here $D_1$ is a reference diffusion coefficient for NaCl or sucrose in water. Consequently, the dimensionless sensitivity function can be written using eqs 15 and 20 as

$$S_i^f(\eta_1; D) = \frac{4}{\tau_{12}' \xi \pi} \sum_{m=0}^{\infty} \frac{1}{2m+1} \sin \left( \frac{(2m+1)\pi}{2} \eta_1 \right) P_m$$

(21)

where

$$P_m = \left\{ \exp(M_1 \xi \tau_1') - 1 \right\} + \exp(M_1 \xi \tau_1')$$

and

$$M_1 = -\frac{(2m+1)^2 \pi^2}{4}$$

In Figure 5, we plot the dimensionless sensitivity ($S_i^f$) as a function of position ($\eta_1$) at different time instants ($\tau_{12}'$). We consider time up to $\tau_{12}' = 17.26$ as, according to Figure 4, constant concentration persists for this time period at the interface between deionized water and sucrose solution. At smaller times, the function $S_i^f$ shows a maximum at an intermediate location that moves toward higher values of $\eta_1$ with increase in time. At later times ($\tau_{12}' > 1.048$), the variation becomes monotonic, reaching a maximum at $\eta_1 = 1$. Eventually, sensitivity decreases uniformly across the test cell.

These trends can be explained in terms of the density variation in the cavity. The initial phase of increasing sensitivity corresponds to a concentration front of the solute traveling from the base of the cavity toward higher values of $\eta_1$. However, at further higher values of $\eta_1$, concentration changes are minimal and cannot yield information on the diffusion coefficient. Consequently, a maximum in sensitivity occurs at an intermediate value of $\eta_1$ and shifts toward higher values as diffusion progresses. At later times, the front reaches the top surface. The increase in concentration with time at the top wall correlates best with the diffusion coefficient. However, the top wall is impermeable to the mass transfer and the concentration levels of the solute in the cavity are redistributed, leading ultimately to a well-mixed solution. Such an approach toward the steady state progressively reduces the sensitivity coefficient. Consequently, in the limit of the steady state the sensitivity function diminishes to zero, as in this limit the profile becomes completely independent of the diffusion coefficient.

Similar to eq 20, the sensitivity function associated with the experimental data can be obtained in time by integrating over a layer thickness as follows:

$$S_1(t; D) = \int_0^{H-h_1} \frac{dp}{dD} \, dy$$

(22)

If dimensionless parameters associated with eq 22 are defined as

$$\xi = \frac{D}{D_1}, \quad \bar{S}_i^f(\tau_1''; D) = \frac{D_2 S_i(\tau_1''; D)}{(H-h_1)(\rho_1 - \rho_0)}$$

and

$$\tau_1'' = \frac{t D_1}{(H-h_1)^2}$$

then eqs 15 and 22 lead to the dimensionless sensitivity function:

$$\bar{S}_i(\tau_1''; D) = 2\tau_1'' \sum_{m=0}^{\infty} \exp \left[ -\frac{(2m+1)^2 \pi^2}{4} \xi \tau_1'' \right]$$

(23)

The cavity-averaged sensitivity function ($\bar{S}_i$) with respect to time is shown in Figure 6. The highest sensitivity is seen once again at an intermediate time instant of 1.048 in dimensionless units. At later times, concentration tends to equalize within the test cell, as a steady state is approached, and the sensitivity coefficient approaches zero.

The above discussion clearly establishes that using analyzable experimental data for which the sensitivity coefficient is very high is the most appropriate way of obtaining the mass diffusion coefficient. Since determination of the mass diffusion coefficient is a nonlinear parameter estimation problem, sensitivity analysis requires an approximate mass diffusivity to initiate numerical calculations. An approximation can be obtained by first working with the entire data set, which can be subsequently refined by examining the sensitivity function.
The use of the sensitivity coefficient for thermal diffusivity was demonstrated by our group in the context of heat conduction in recent publications. However, owing to the following important differences between the heat and the mass transfer measurements, the analysis of the latter tends to be more cumbersome:

i. Boundary conditions in the mass transfer experiments are usually zero flux, while they are usually constant temperature for the heat transfer experiments. Therefore, the analytical solutions for the two experiments are different.

ii. In a mass transfer experiment, steady state is approached by a redistribution of solute in the solution resulting in multiple time scales. In a heat transfer experiment, on the other hand, the hot and cold boundaries establish a steady heat flux through the medium. The resulting time scale is therefore unique.

iii. The mass diffusion coefficient is usually much smaller than thermal diffusivity.

iv. Finally, the change in refractive index with species concentration is much larger than that with temperature.

Factors iii and iv yield a very large number of fringes in mass transfer, making fringe analysis cumbersome. In addition, the refraction errors are expected to be significant over a longer period of time. In heat transfer, the fringe density is initially high and the refraction errors fade away over a shorter period of time. Consequently, analysis of the data in those respective regions in space and time, where a large number of fringes exist and are prone to have large refraction errors, becomes practically impossible even though the sensitivity coefficient may have a large value in that region. We therefore conduct analysis by fitting the analytical solution to practically analyzable data, which has maximum sensitivity.

In the analytical solution given by eq 15, we consider mass diffusivity as a constant property since an analytical solution of the diffusion equation is not possible with concentration dependent diffusivity. This difficulty can be circumvented by a numerical technique for solving the governing differential equation. Furthermore, the sensitivity coefficient is also obtained by numerically evaluating the integral in eqs 20 and 22. For maintaining clarity, we have worked with a constant mass diffusivity in the present study wherein an analytical expression is possible for the sensitivity coefficient. The analytical solution is fitted to that data in space and time for

![Figure 7. Evolution of interference pattern as a function of time for diffusion of 30 wt % aqueous solution of sucrose in deionized water at 25 °C and \( h_1 = 8.23 \) mm. Data analysis is based on the fringe patterns recorded at different time instants.](image-url)
which sensitivity is a maximum. It can be seen from Figure 10 that the analytical solution fits the data very well in the high sensitivity region, suggesting that diffusivity is weakly dependent on concentration over a concentration window associated with high sensitivity.

5. RESULTS AND DISCUSSION

In mass transfer experiments, we have used two systems, namely, sucrose solution with 5, 15, 30, and 50 wt % concentration and NaCl solution of 5, 15, and 26 wt % concentration. The concentrations of solute in both solutions, prepared in ultrapure water, are below their respective solubility limits. Before starting the experiment, the solution of a certain concentration is placed at the base of pure water, which initiates mass diffusion at the solution–solvent interface. We record interferograms of the concentration front, using the Mach–Zehnder interferometer as a function of time for over 36 h in each experiment. We analyze the fringes using the two different approaches described in section 3. A least-squares functional that compares the analytical solution of concentration with the experimental measurements yields the diffusion coefficients of sucrose and NaCl in water at an average concentration prevailing in the test cavity over a band where the fringes are distinguishable and the sensitivity is the highest. Equations 21 and 23 are used to examine the sensitivity coefficients for a given thickness of the solution layer over time.

Figures 7 and 8 show, respectively, the evolution of interference patterns during the diffusion of 30 wt % aqueous solution of sucrose and 26 wt % aqueous solution of NaCl in distilled water. The initial layer height of the sucrose solution is 8.23 mm, that of the NaCl solution is 8 mm, and the cavity height in both cases is 50 mm. The fringes initiate at the interface of the solution with water, and they progressively move in the positive y direction. The movement of the front (front speed) is observed to be sluggish, which is a characteristic feature of the slowly diffusing systems under study. A large number of fringes, particularly closer to the interface, is a consequence of the slow change in density from one fringe to the next is given by eq 3. It accounts for the phase shift in the test beam due to the change in refractive index compared to that of the reference beam. However, it does not account for the effect of beam bending. Light refraction is expected to be large near the initial solution–solvent interface; however, that region is excluded by the sensitivity coefficient approach considered in the present work. The density at the first fringe closer to the top of the interferogram is that associated with pure water. Consequently, by fringe counting, the entire concentration field can be determined at each time instant. In Figure 9, a typical method used for fringe counting is demonstrated as discussed in section 3.

Figure 10 shows a plot of the sucrose concentration as a function of position at various time instants within a single experiment. It can be seen that we have obtained the data at different times only up to 11 fringes from the top. This is because the fringes beyond this value are densely spaced. According to Figure 5, the distinguishable fringes toward the smallest value of $\eta_1$ shown in Figure 10 have the maximum sensitivity. In addition, as shown in Figure 6, the longest time at which the data is obtained over the explored time interval yields the data with maximum sensitivity. We therefore fit the analytical solution given by eq 15 through the minimization of error in eq 16, in such a fashion that it fits the available data.
having maximum sensitivity the best. Such a fit also justifies the usage of a constant value of diffusivity as discussed before.

In Figure 10 we represent the fit by solid lines. Overall, the match is seen to be excellent toward the higher sensitivity zone in the band of distinguishable fringes. The departure between the analytical solution and experimental results is seen at short times and closer to the interface, where refraction errors are likely to be significant. As suggested by the sensitivity analysis, the match between the experimental results and the analytical solution improves as time passes.

The uncertainty in the parameter estimated from a full interferogram depends on the time instant considered and the number of fringes included under the summation sign of eq 16. It can be associated with the sharpness with which the error functional \( \varepsilon \) attains a minimum when the parameter is continuously varied. Figure 11 shows this variation for the data shown in Figures 7 and 10 at selected time instants. It can be seen that the least-squares error progressively decreases with time, reaches a minimum, and then increases at very long times. The data of Figure 10 is consistent with Figure 6 for the sensitivity function that attains a maximum within the time window and beyond which the interfacial concentration starts to change.

We also carried out the analysis similar to Figures 10 and 11 for the diffusion of NaCl for which the interference patterns are shown in Figure 8. The mass diffusion coefficients for both systems obtained by including sensitivity analysis are plotted in Figure 12. It is seen that mass diffusivity increases with the initial concentration of the solute-rich phase. The experimentally determined values match very well with those available in the literature (Table 1). Furthermore, the trend observed...
It should be noted that these parameters are only apparatus plotted in Figure 14) as from Figure 8 (for which the velocity of the sixth fringe is understandable because of the increase in sensitivity of sucrose) has yielded parameters closest to the literature. This is Predictions with late-time data (>100 min for both NaCl and choice of the time interval was found to be important. Equations with late-time data (>100 min for both NaCl and sucrose) has yielded parameters closest to the literature. This is understandable because of the increase in sensitivity of interferograms with the passage of time as shown in the inset of Figure 6. The model parameters for NaCl were obtained from Figure 8 (for which the velocity of the sixth fringe is plotted in Figure 14) as \( y_0 = 4.303, a = -3.645 \), and \( b = 2.542 \). It should be noted that these parameters are only apparatus specific, and therefore can be used for the data analysis with other solute–solvent combinations in the cavity.

For various concentrations of sucrose and NaCl in the initial solution, we plot the position of the sixth fringe along the \( y \) coordinate of the test cell at various time instants in Figure 13.

For both solutions the fringe speed can be seen to be decreasing with an increase in time. The mass diffusion coefficient was obtained by fitting eq 19 to the data given in Figure 13. The best fit to the sucrose data is shown as a solid line in Figure 14. In Figure 15 we plot the least-squares error for various sucrose concentrations with respect to the diffusion coefficient as an independent variable. It can be seen that a clear minimum is attained within the range of interest. We also carried out a similar analysis for NaCl solution. The mass diffusivities of NaCl and sucrose in water as a function of initial concentration are plotted in Figure 12. The predictions of the single fringe approach are seen to be comparable to those from the full interferograms.

The mass diffusion coefficient data obtained from the two approaches plotted in Figures 12 are consistent with each other and show an increase with concentration. Furthermore, the disparity in mass diffusion coefficients calculated from the two approaches is small and is essentially due to the difference in diffusivity obtained from the full fringe analysis and the reference value considered in the single fringe analysis. We also fit a quadratic function to the diffusion coefficient as a function of the initial weight percent of the solute in water. The coefficients of the quadratic are summarized in Table 2 and are seen to match well with the literature.

Finally, it should be noted that the full interferogram analysis approach is the most detailed and is recommended when good quality interferograms are available. It requires that fringe minima be determined with accuracy. In this method, the measurement data is fitted to the analytical solution of a model equation of classical mass diffusion. The second approach, on the other hand, relies on calibrating a setup for a known solute diffusing in a solvent and is rapid. The calibration curve combined with data on the fringe position with time is adequate for determining the diffusion coefficient. The second method is preferred when the uncertainty in locating the fringe position is expected to be large, for example, in diffusion of colloidal suspensions in water, where owing to large density

Figure 13. Position of the sixth fringe along the \( y \) coordinate of the test cell at various time instants for diffusion of NaCl and sucrose in deionized water at 25 °C. The filled symbols represent position data obtained for sucrose, while the open symbols represent those obtained for NaCl.

Figure 14. Speed of the sixth fringe calculated from nonlinear regression as a function of time for diffusion of sucrose in deionized water.

Figure 15. Variation of logarithmic error during measurement of mass diffusion coefficient of sucrose in water at 25 °C. It can be seen that a progressive shift in the predicted diffusion coefficient shifts to the higher values with increase in initial concentrations.

Table 2. Quadratic Fit of Mass Diffusion Coefficient against Initial Solute Concentration of NaCl and Sucrose Diffusing in Distilled Water at 25 °C (Figure 12)

<table>
<thead>
<tr>
<th>method</th>
<th>( D = a_0 + a_1C + a_2C^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>full interferogram</td>
<td>( a_0 = 1.252 ) ( a_1 = 0.0124 ) ( a_2 = -1.7 \times 10^{-4} )</td>
</tr>
<tr>
<td>propagation of fringes</td>
<td>( 1.333 ) ( 0.00513 ) ( 4 \times 10^{-3} )</td>
</tr>
<tr>
<td>Rard et al.(^{19} )</td>
<td>( 1.477 ) ( 0.003 ) ( 12 \times 10^{-5} )</td>
</tr>
<tr>
<td>Chang et al.(^{20} )</td>
<td>( 1.466 ) ( 0.007 ) ( -9.5 \times 10^{-5} )</td>
</tr>
<tr>
<td>sucrose</td>
<td>( 4.08 ) ( 0.0235 ) ( -1.84 \times 10^{-4} )</td>
</tr>
<tr>
<td>full interferogram</td>
<td>( 4.211 ) ( 0.353 ) ( -3.18 \times 10^{-4} )</td>
</tr>
</tbody>
</table>

6. CONCLUSIONS

In this work the experimental determination of the mass diffusion coefficient using a Mach–Zehnder interferometer through sensitivity analysis is discussed. A large variation in the sensitivity coefficient suggests that the analytical solution should be fitted to the appropriate portion of the experimental data for reliable determination of diffusivity. For the configuration considered, a longer time period data within the constant interfacial concentration time window shows high sensitivity and is the best from the viewpoint of parameter estimation. On the other hand, location of the high sensitivity region in space depends upon the time of measurement. Owing to experimental constraints such as distinguishability of fringes, refraction errors, or very large measurement times, obtaining experimental data in space and time that has the absolute maximum in sensitivity is not feasible. Therefore, that part of the experimental data is studied that has large sensitivity and is practically analyzable. Two fringe analysis techniques are compared in terms of the least-squares error and uncertainty in the predicted mass diffusivity. The first works with the full interferogram and is the most detailed. It requires high quality optical images from which the light intensity minima can be correctly determined. The second approach calibrates the measurement against a known diffusing solute. It can then be rapidly used for other solute—solvent combinations. Both techniques show good quality predictions of the diffusion coefficients for sucrose and NaCl in water over a range of concentrations.

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Notes
The authors declare no competing financial interest.

REFERENCES


